Operating Experience of a 50 kW_{th} Chemical Looping Combustion Rig at NETL: Insight for Scaleup

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What is Chemical Looping Combustion?

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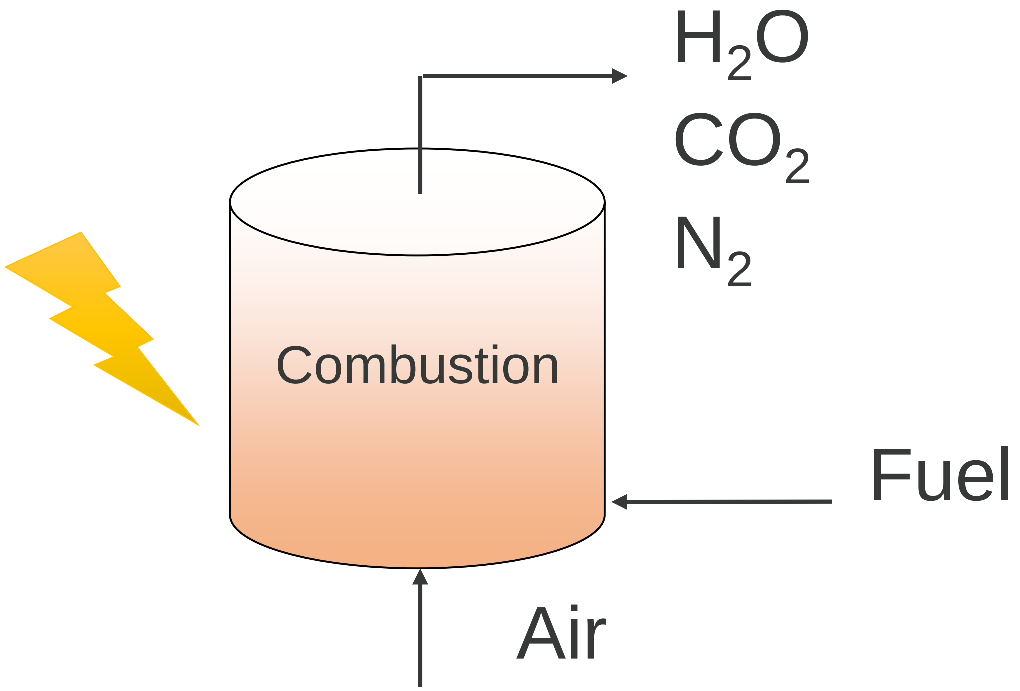
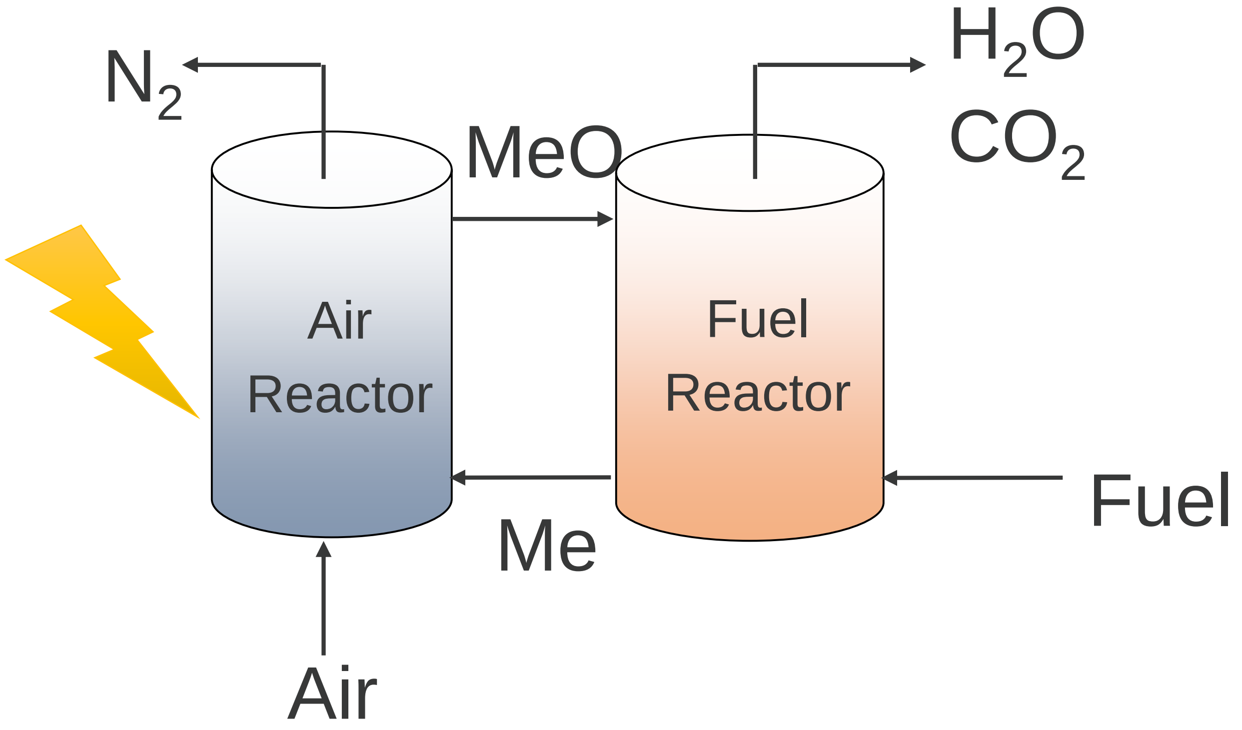
Traditional Combustion



Fuel and air are mixed together and produce energy for electricity generation.

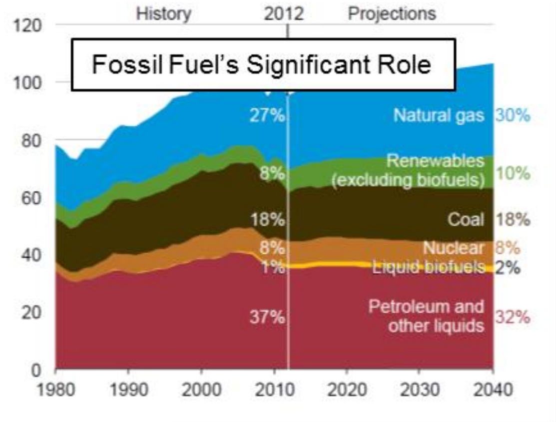
Chemical Looping Combustion



Fuel and air are reacted separately in two stages using an **oxygen carrier**, which is usually a **metal oxide** (MeO). Energy is recuperated in the air reactor step.

Motivation to Study CLC

- **Greenhouse gas emission reduction goals set by Obama**
- **Domestic importance of fossil fuels**
  - Need fossil fuel options that produce minimal GHGs
- **CLC technology has "potential" to achieve DOE goals**



4 – Early Release

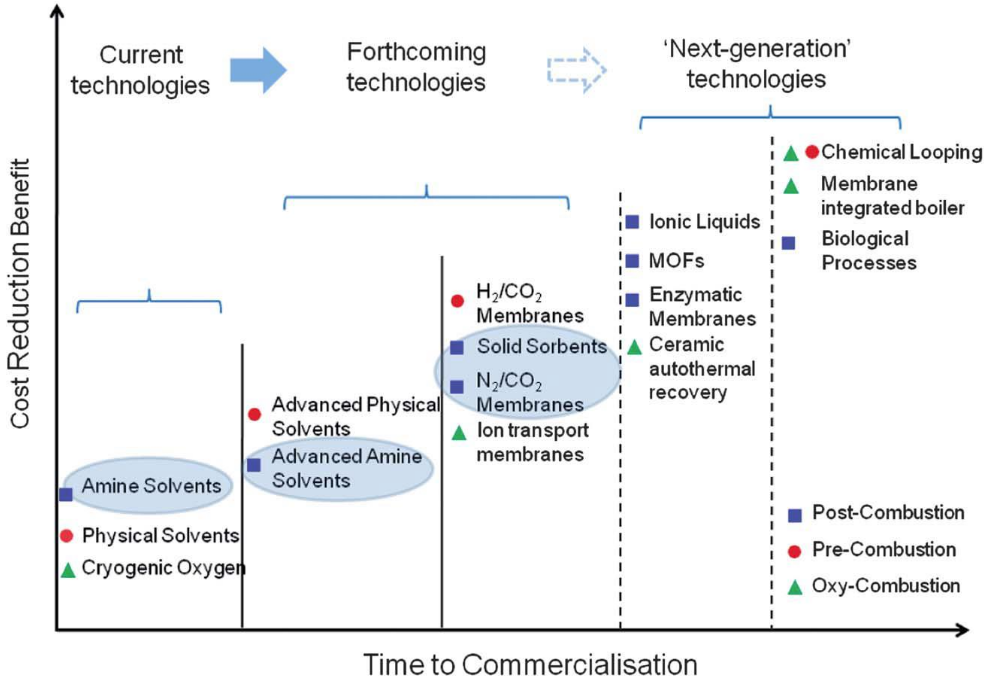


Exhibit ES-3 Cost of electricity breakdown comparison

Cost	Fe_2O_3 ($/MWh)	$CaSO_4$ ($/MWh)	Conventional PC BBR Case 12
Capital	49.6	53.4	73.1
Fixed	11.3	12.2	15.7
Variable	25.7	8.4	13.2
Maintenance materials	3.2	3.5	4.7
Water	0.4	0.4	0.9
Oxygen carrier makeup *	18.7	1.1	N/A
Other chemicals & catalyst	1.9	1.7	6.4
Waste disposal	1.4	1.7	1.3
Fuel	28.4	30.8	35.3
Total	115.1	104.7	137.3

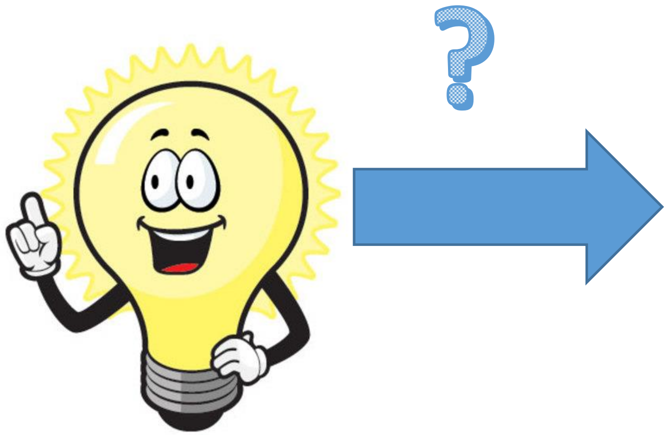
*Fe_2O_3 oxygen carrier makeup: 132 tons/day @ $2,000 per ton; Limestone carrier makeup: 439 tons/day @ $33.5 per ton

Ref: U.S. Department of Energy (DOE), National Energy Technology Laboratory (NETL). Guidance for NETL's Oxycombustion R&D Program: Chemical Looping Combustion Reference Plant Designs and Sensitivity Studies. Pittsburgh : s.n., 2014. DOE/NETL-2014/1643

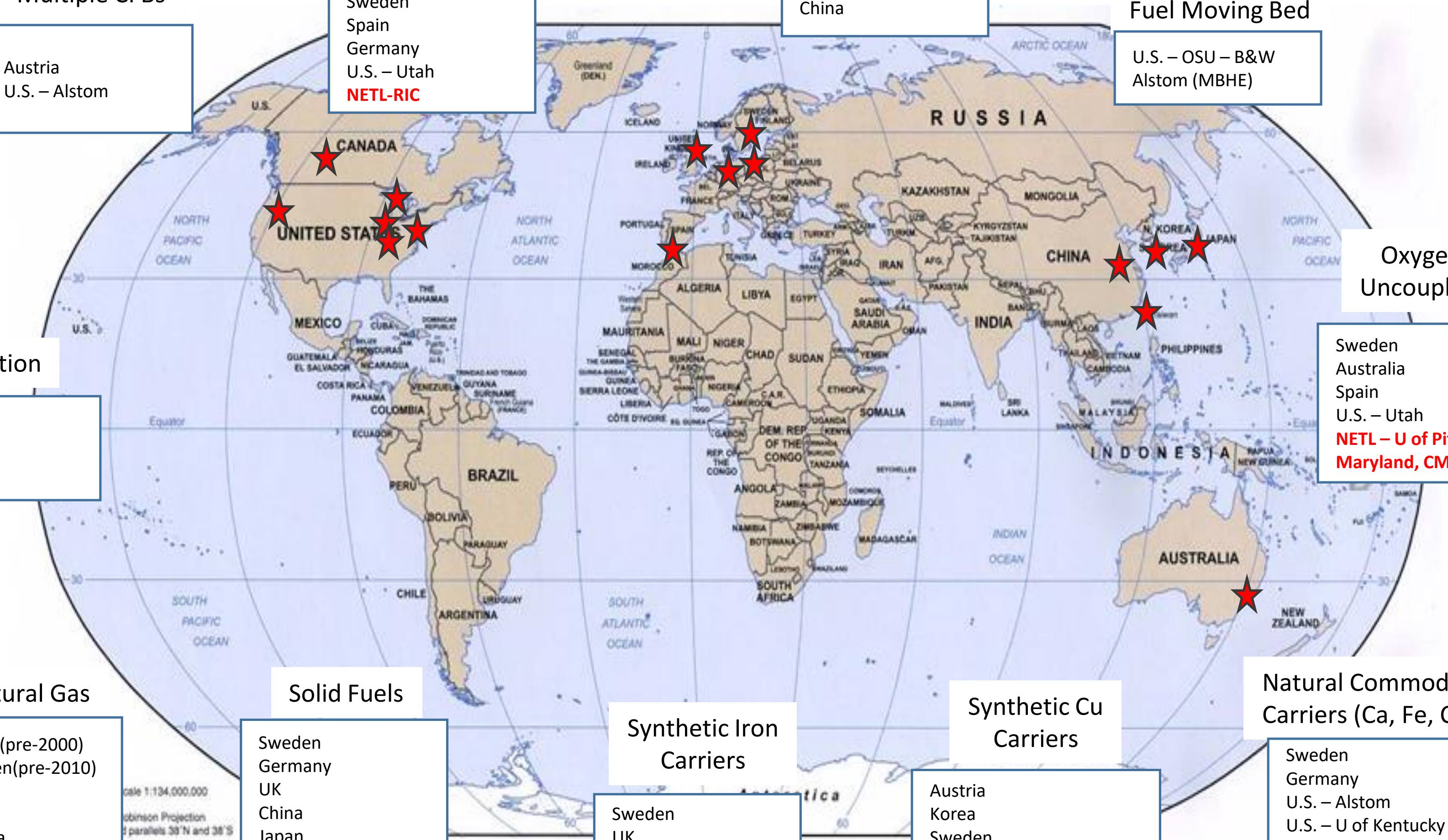
Motivation to Study CLC

What is our end goal?

- **Determine if CLC is a feasible technology and worthy of additional investment/development**
  - →Data and information for strategic decision making
- **If it is feasible, THEN**
  - Help developers overcome technical issues
  - Help technology be successful
  - Ultimately commercialization
  - → jobs and growth



CLC – Worldwide Interest



Multiple CFBs

Austria
U.S. – Alstom

Air CFB/ Fuel BFBR

Korea??
Sweden
Spain
Germany
U.S. – Utah
NETL-RIC

Air CFB/ Fuel Spouted FBR

China

Fuel Moving Bed

U.S. – OSU – B&W
Alstom (MBHE)

Attrition

Canada
UK
UNDakota
NETL-RIC

Oxygen Uncoupling

Sweden
Australia
Spain
U.S. – Utah
NETL – U of Pitt, Maryland, CMU

Natural Gas

Japan (pre-2000)
Sweden(pre-2010)
Korea
Spain
Austria
NETL-RIC

Solid Fuels

Sweden
Germany
UK
China
Japan
U.S. – Alstom
U.S. – OSU-B&W
U.S. – U of Kentucky
U.S. – Utah

Synthetic Iron Carriers

Sweden
UK
China
U.S. – OSU-B&W
NETL-RIC

Synthetic Cu Carriers

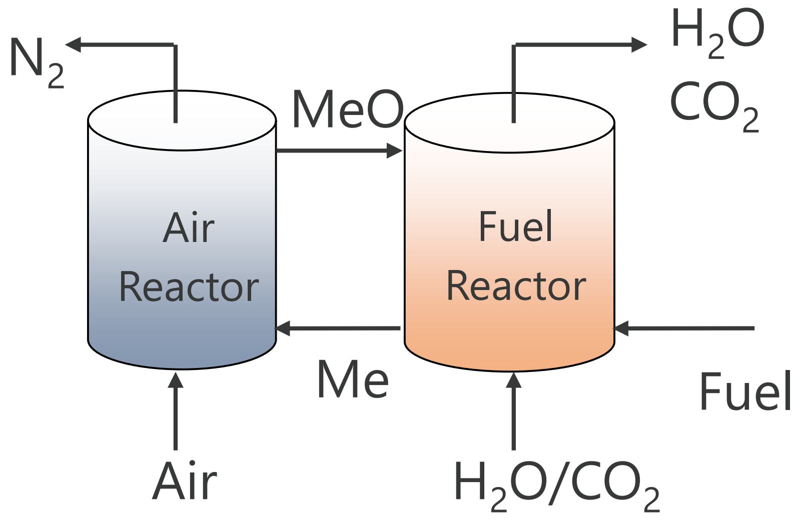
Austria
Korea
Sweden
Spain
U.S. – Utah
NETL-RIC

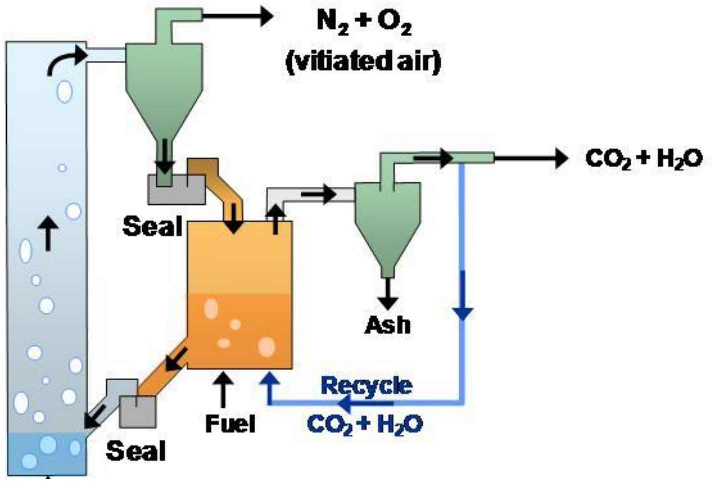
Natural Commodity Carriers (Ca, Fe, Cu)

Sweden
Germany
U.S. – Alstom
U.S. – U of Kentucky
U.S. – Utah
Taiwan – ITRI
NETL-RIC

List of challenges

- **Find a good oxygen carrier**
  - Must withstand many oxidation/reduction cycles and attrition
- **Reactor design**
  - Must effectively convert most of the fuel into CO_2 and Steam
- **Solids handling**
  - Smoothly move solids between reactors at high temperatures and pressures
  - Control solids flow rate
  - Prevent product gases from mixing!





Chemical Looping at NETL

Component Development

- Experimental (cold models)
- Simulations (MFIX, Barracuda)

Chemical Looping Reactor

System Studies

Cost	Fe_2O_3 (\$/MWh)	$CaSO_4$ (\$/MWh)	Conventional PC BBR Case 12
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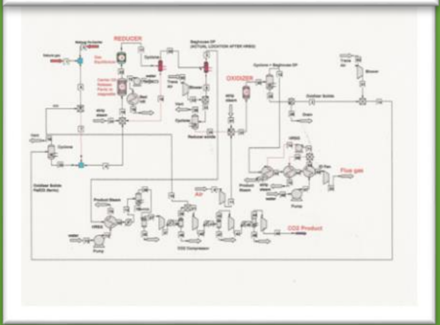
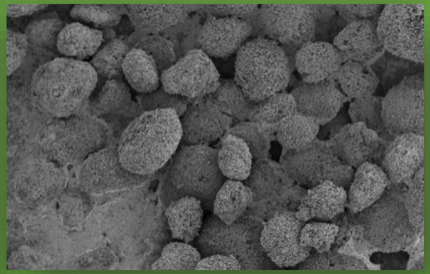
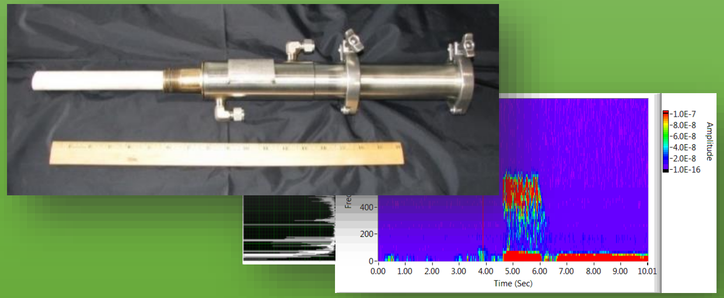


Oxygen Carrier Performance and Durability

- Reactivity
- Strength/Attr.
- Characterization

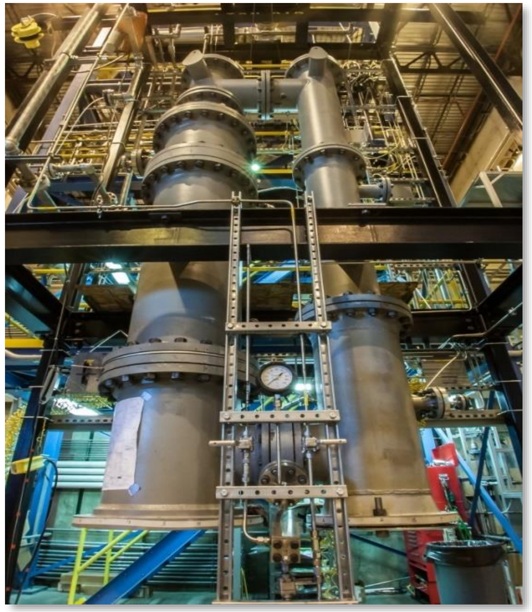


Sensor Development



- Gas composition
- Solids flowrate

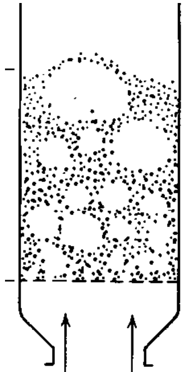
Chemical Looping "Reactor"

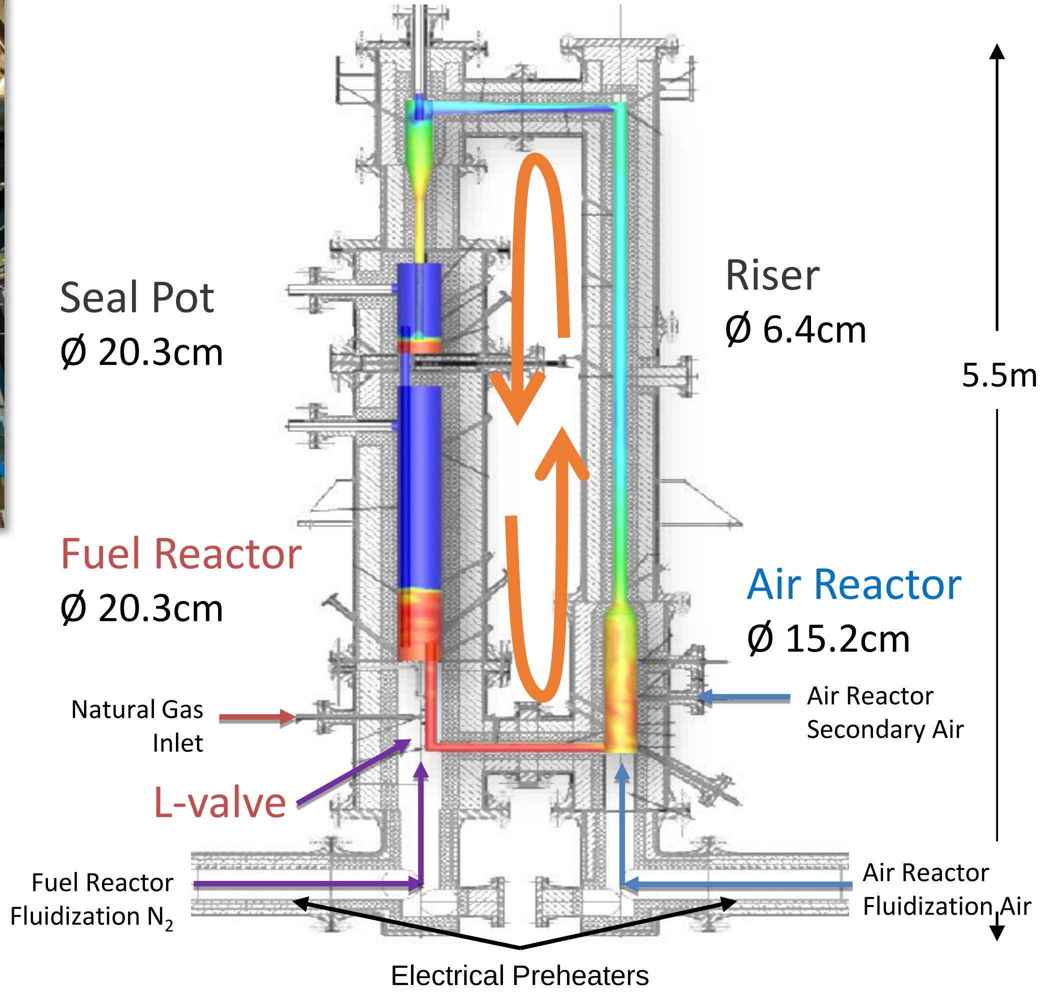


Capacity: 50 kW_{th} natural gas

Configuration:

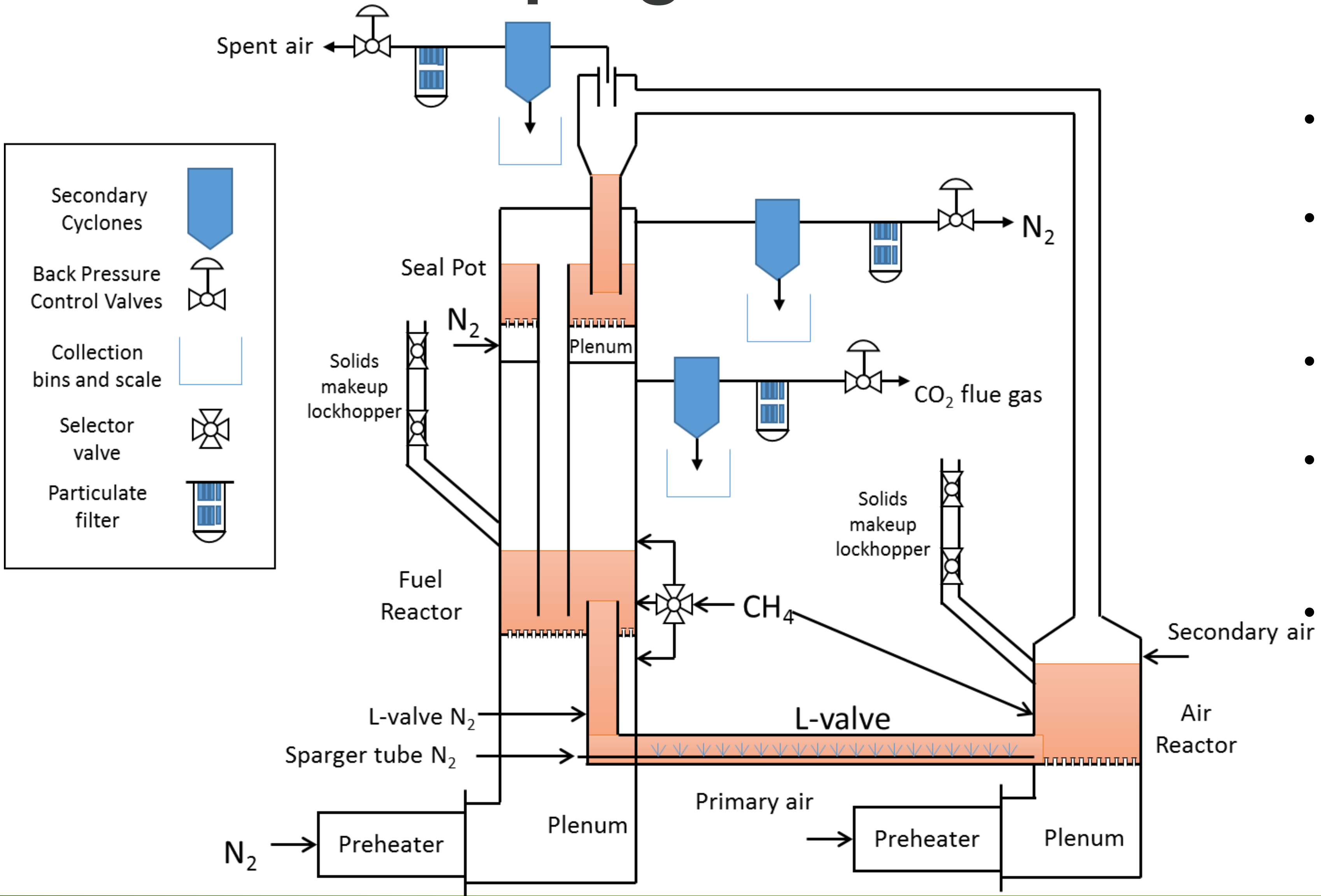
- Fuel Reactor – Bubbling Bed
- L-valve – to control solids circulation rate
- Air Reactor – Turbulent, transporting bed
- Riser – conveys particles
- Seal Pot – Prevents air from entering the fuel reactor and vice versa





- Vessels are refractory lined carbon steel
- Internal temperature 800-1000°C
- Heated up with electric gas preheaters and natural gas combustion
- Heat loss presents a challenge at this scale, since surface-area/volume ratio is fairly large.
  - Natural gas added to air reactor to ensure fuel reactor temperature is high

Chemical Looping "Reactor"



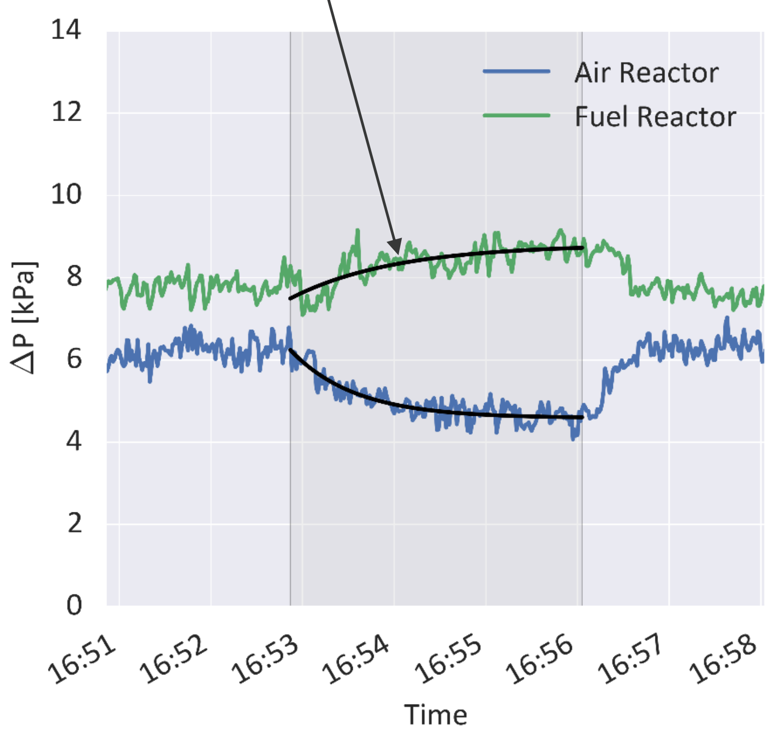
- Secondary cyclones capture fines ejected from reactors
- These solids are collected and weighed occasionally to gather info about attrition rate
- Solids makeup hoppers for adding carrier
- Gases measured using infrared analyzer, gas chromatography

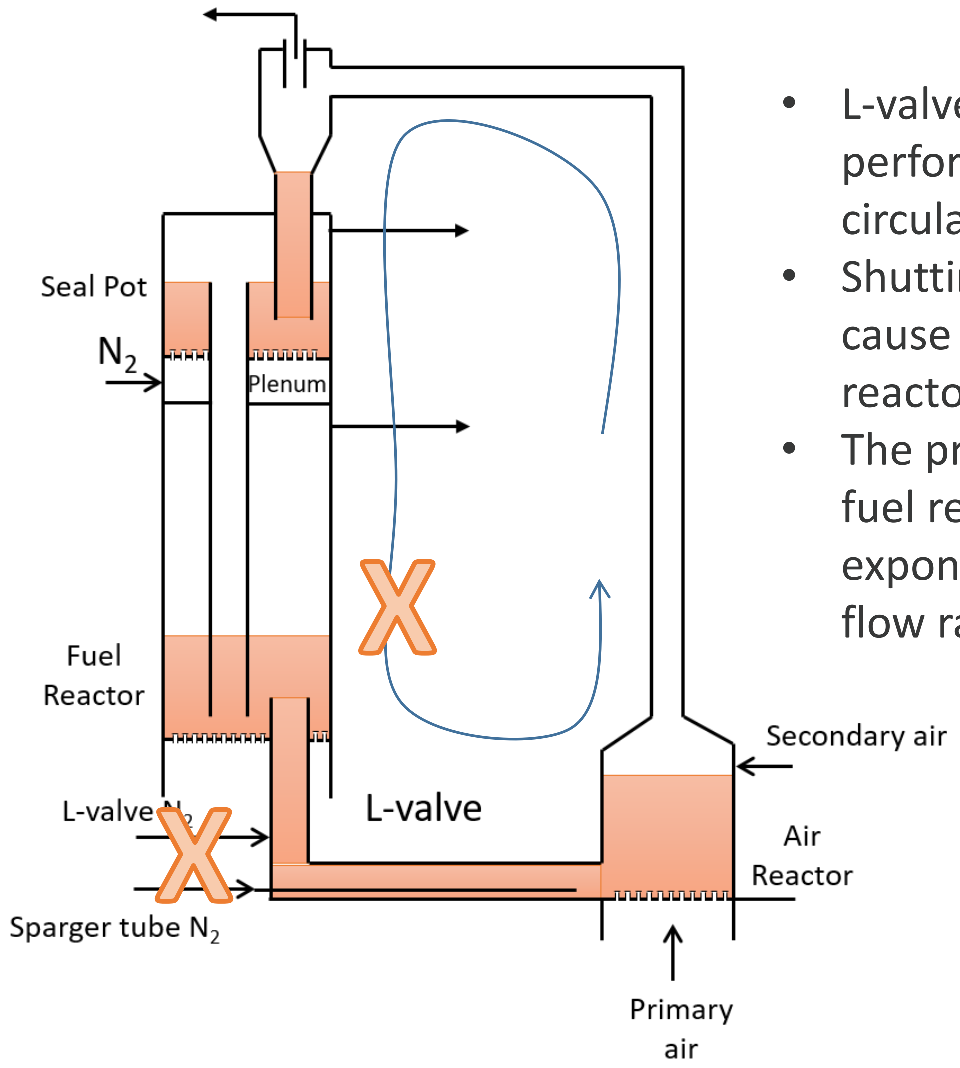
- Backpressure control valves
  - Global pressure: 8 psig

Determination of Solids Circulation Rate

$$\frac{dm}{dt} = \frac{A}{g} \cdot \frac{dP}{dt}$$

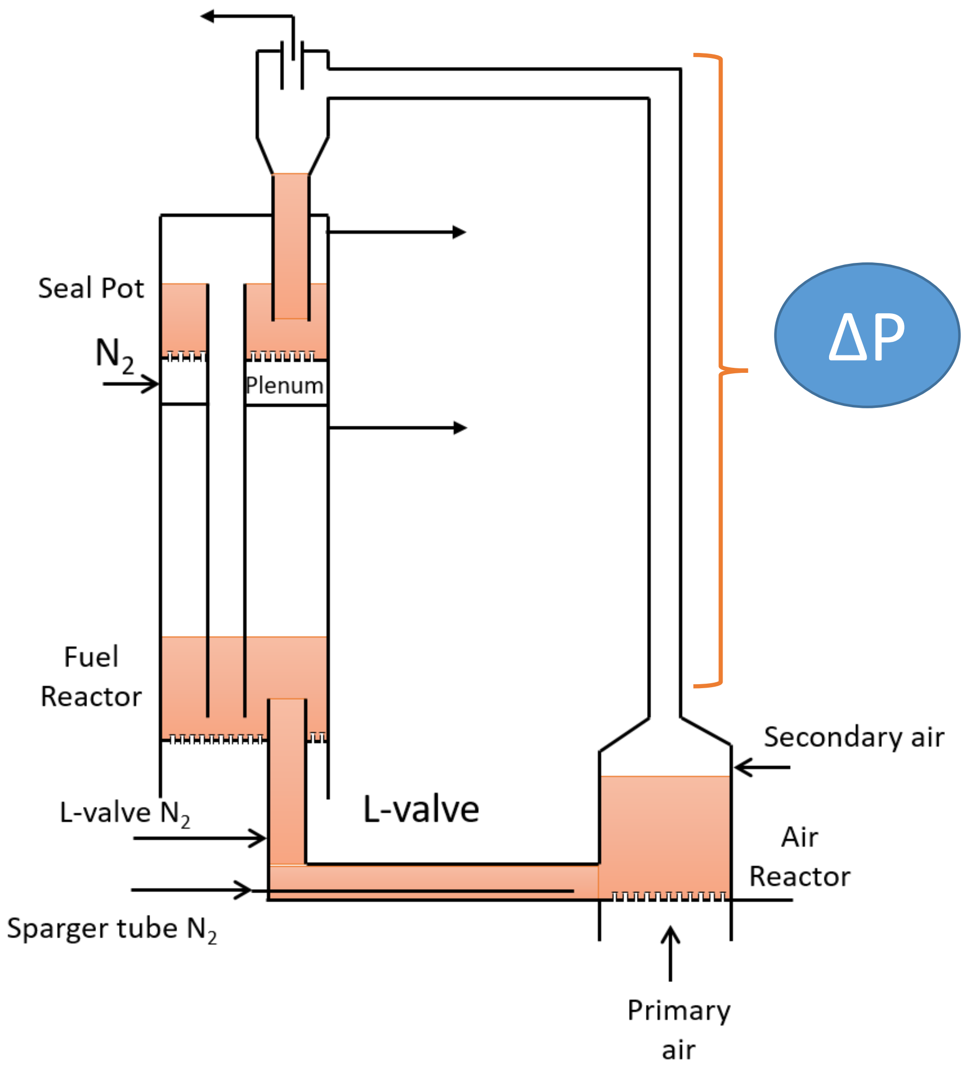
$$\Delta P(t) = P_1 + (P_0 - P_1)e^{-k(t-t_0)}$$



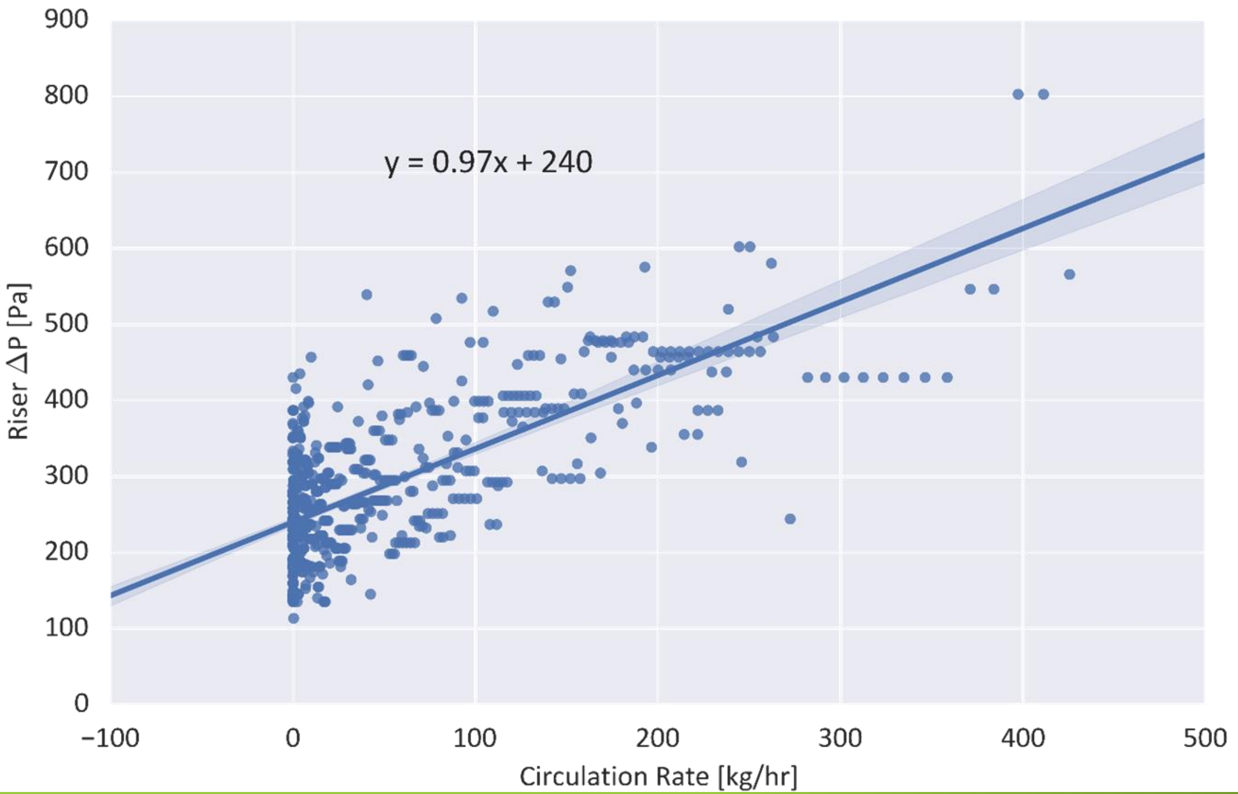


- L-valve cutoff tests were performed to measure the solids circulation rate
- Shutting off L-valve aeration gases cause solids to build up in fuel reactor and exit the air reactor
- The pressure drop in the air and fuel reactors can be fit to an exponential to determine solids flow rate

Circulation Rate Estimation Correlation



- Correlation created from riser pressure drop data and the calculated circulation rate from the L-valve cutoff tests
- Used for finding solids flow rate during trials based on riser pressure drop
- Standard error of data results in confidence of +/- 50 kg/hr

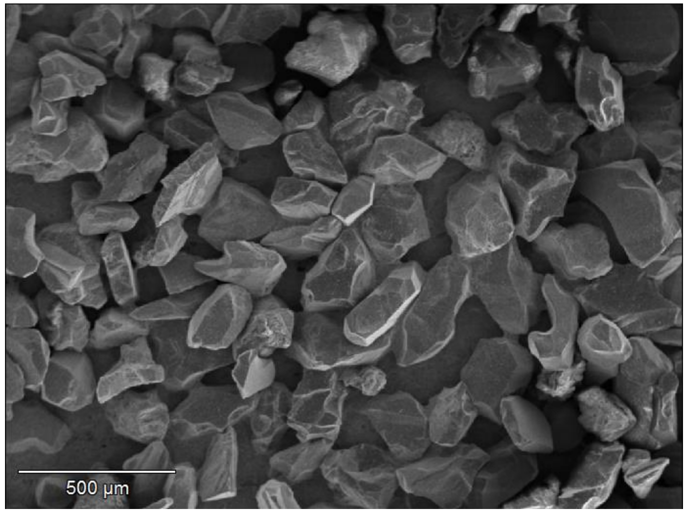


Bayham, S., Straub, D., and Weber, J., "Operation of the NETL Chemical Looping Reactor with Natural Gas and a Novel Copper-Iron Material," NETL-PUB-20912; NETL Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Morgantown, WV, 2017

Carriers tested in CLR

	Hematite	Promoted Hematite	Synthetic Cu-Fe	
Particle density	4.9	4.9	2.9	g/cm3
Sauter Mean Diam.	210	210	343	µm
D50	238	238	397	µm
Sphericity	0.876	0.876	0.91	--
Umf (at 298 K)	8.55	8.55	14	cm/s
Fe_2O_3	86.6%		31%	
CuO			37%	
“Inert”	13.4%		31%	

- Hematite is a strong carrier
- Cheap!
- Poor reactivity with methane



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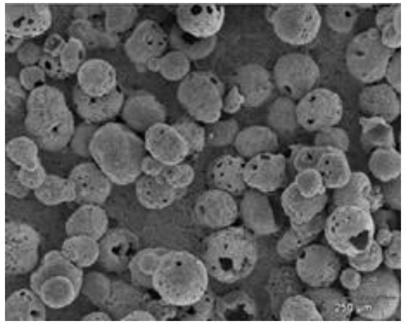
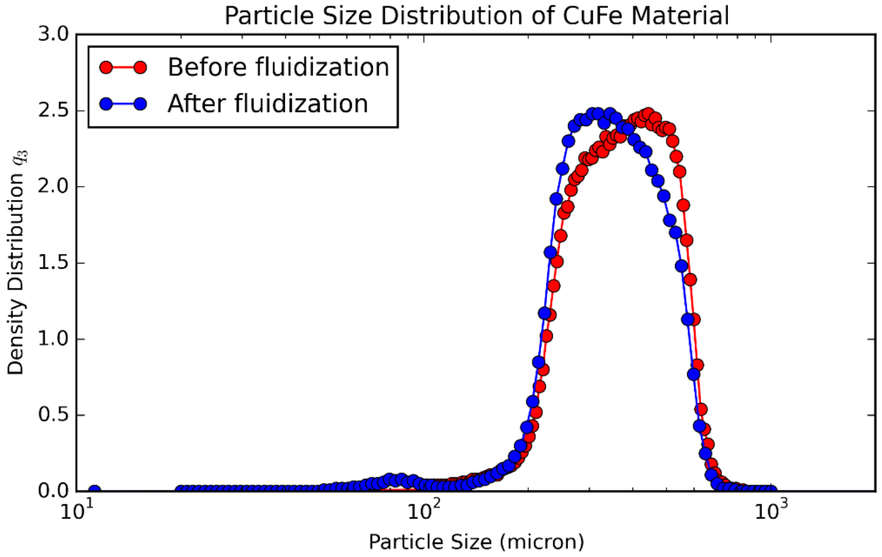
Fe_2O_3	86.6%		31%		
CuO			37%		
“Inert”	13.4%		31%		

- Excellent reactivity
- Scaled up to ~400 kg batch by Nextech
- Fresh material exhibited attrition by abrasion





Fuel Reactor – Air Reactor Temp Differential

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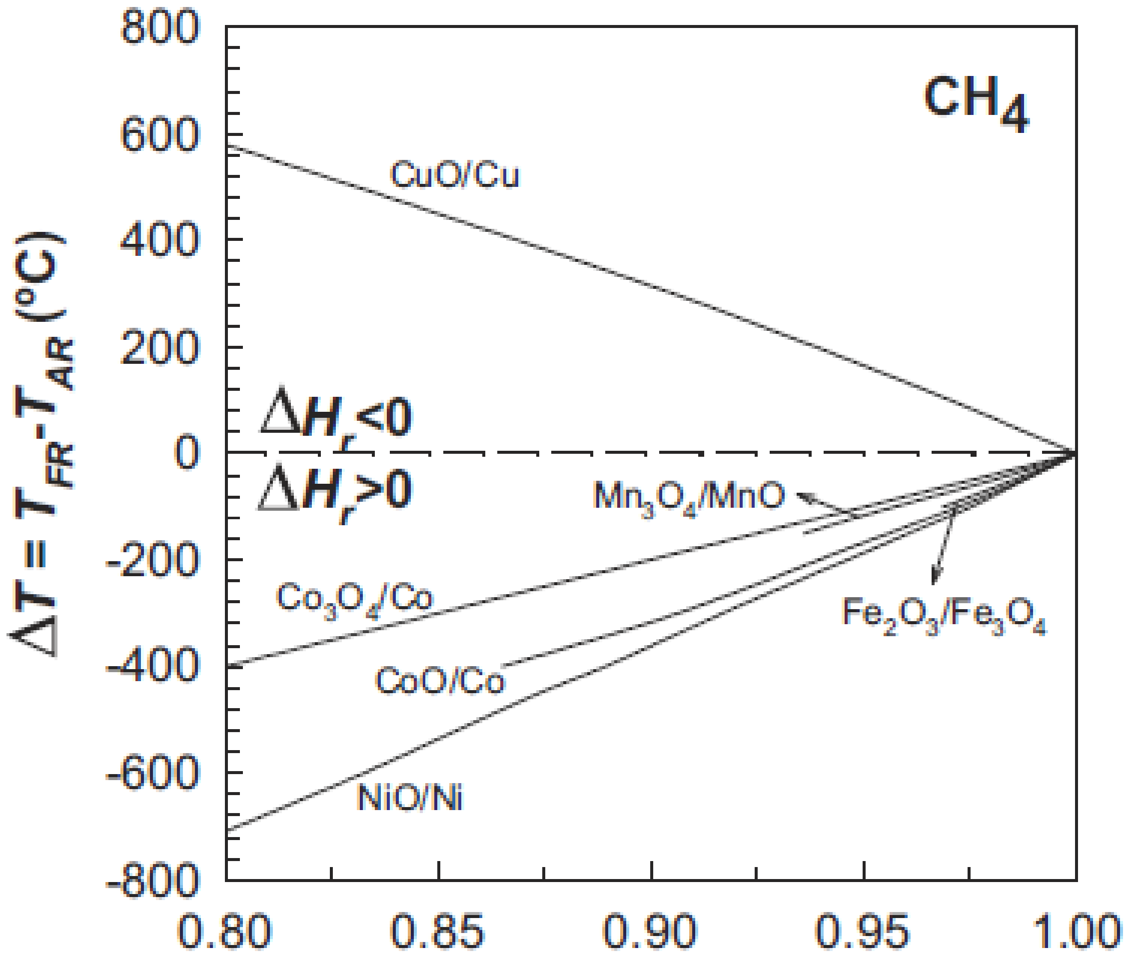
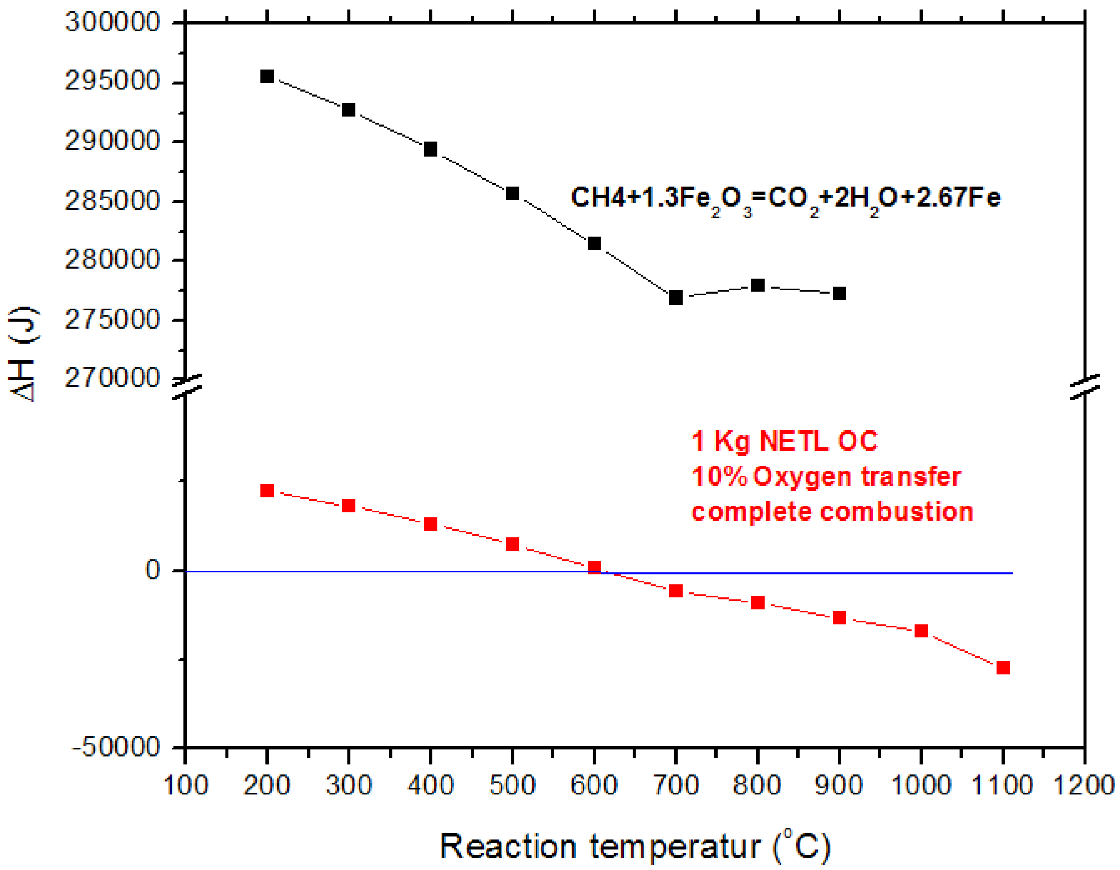


Oxygen Carrier Conversion

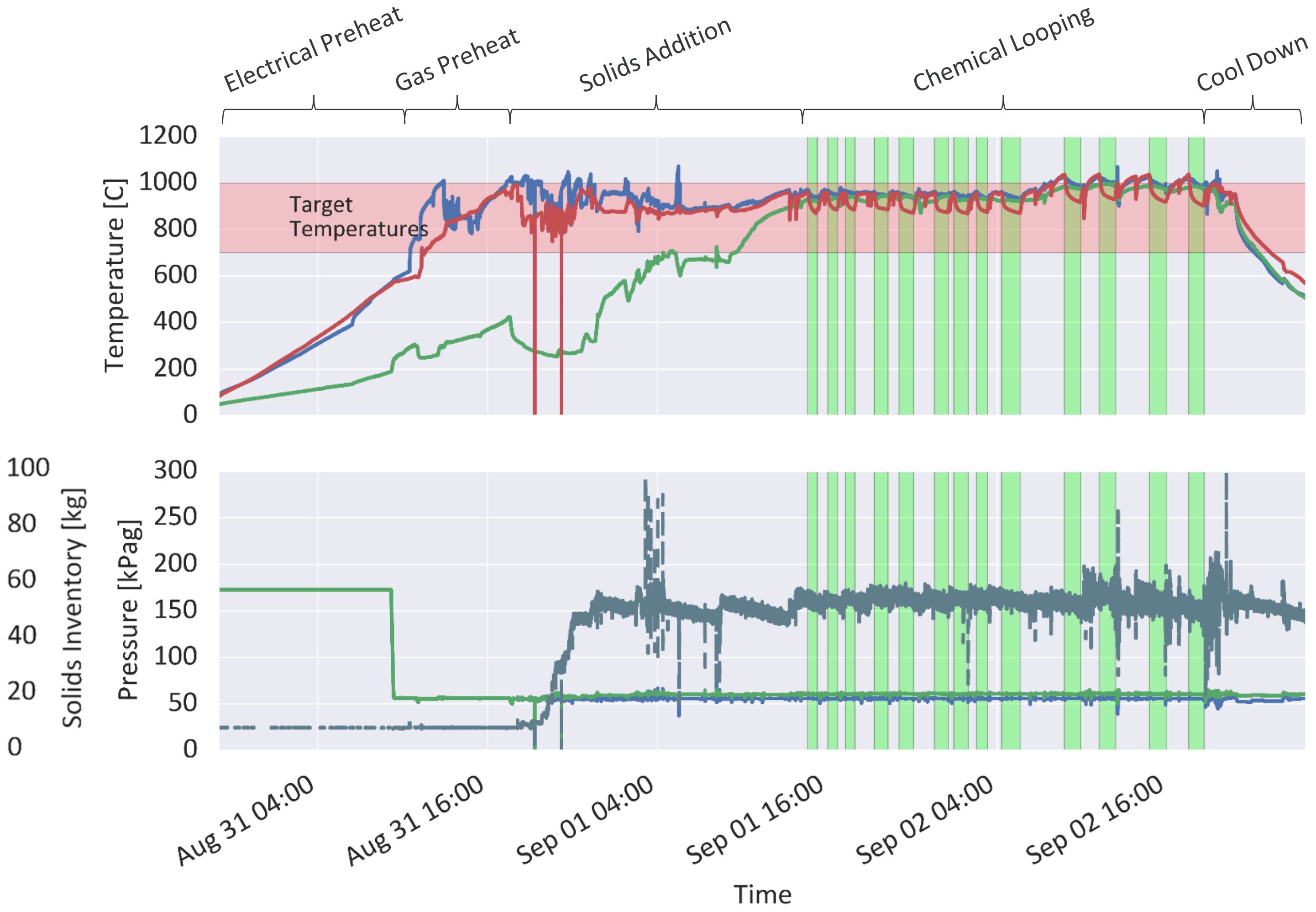
Adanez et al. Prog. Energy Combust Sci. 38 (2012) 215-282c



- CuO-Fe_2O_3-Al_2O_3 reduction is exothermic above 600 ^0C
  - Exothermic reduction reaction is advantageous
  - Minimal heat transfer necessary from the oxidizer

Siriwardane et al. "Pilot Scale (50kW$_{th}$) Chemical Looping Combustion Tests with Commercially Prepared CuO-Fe_2O_3-Alumina Oxygen Carrier." *Presented at the 4th Int'l. Conf. in Chemcal Looping*, Nanjing, China, 2016.

Hematite Carrier Test Campaign

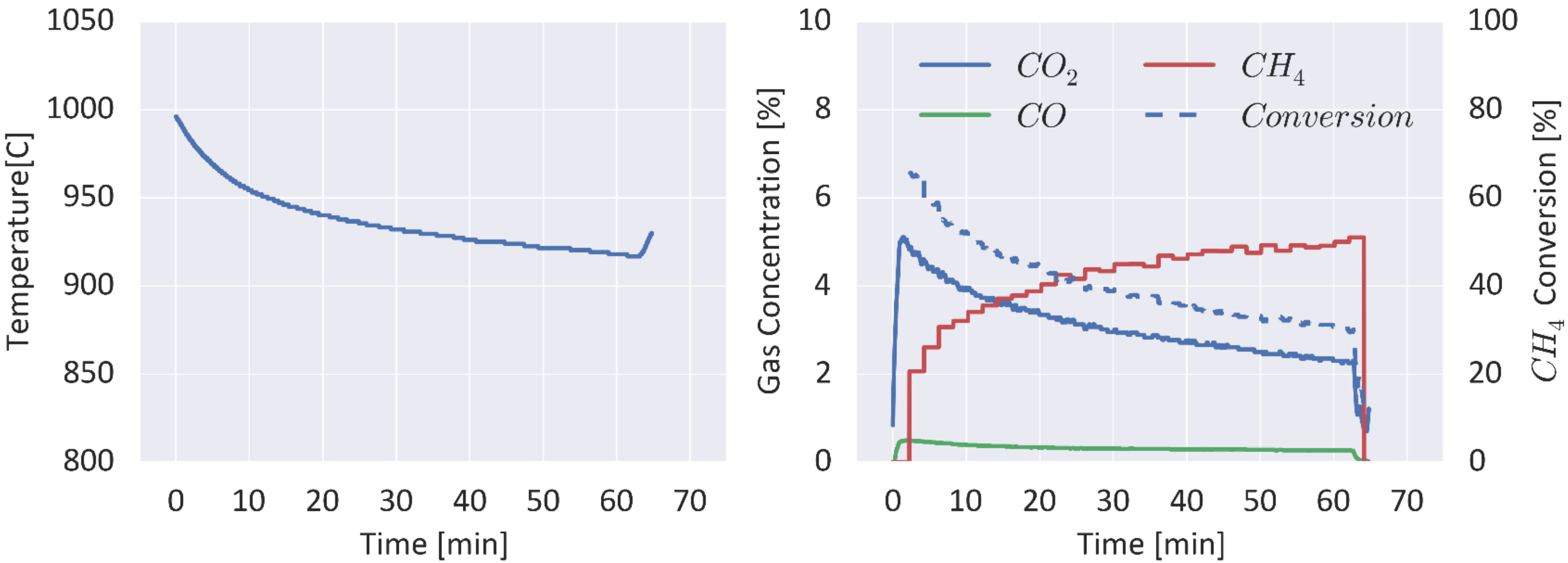


Test Duration: 3 days, 4 hours and 48 minutes

- 13 chemical looping tests periods
- 12.8 hrs of chemical looping
- Circulation rates ranged from 387 to 434 kg/hr
- Carbon balance ranged from 89 – 99%
- Methane conversion between 9-35%

Weber, J.; Straub, D.; Bayham, S.; Breault, R.W., 2016. Operating Experience of a 50kWth Methane Chemical Looping Reactor. Proceedings of Fluidization XV, Montebello Quebec, Canada.

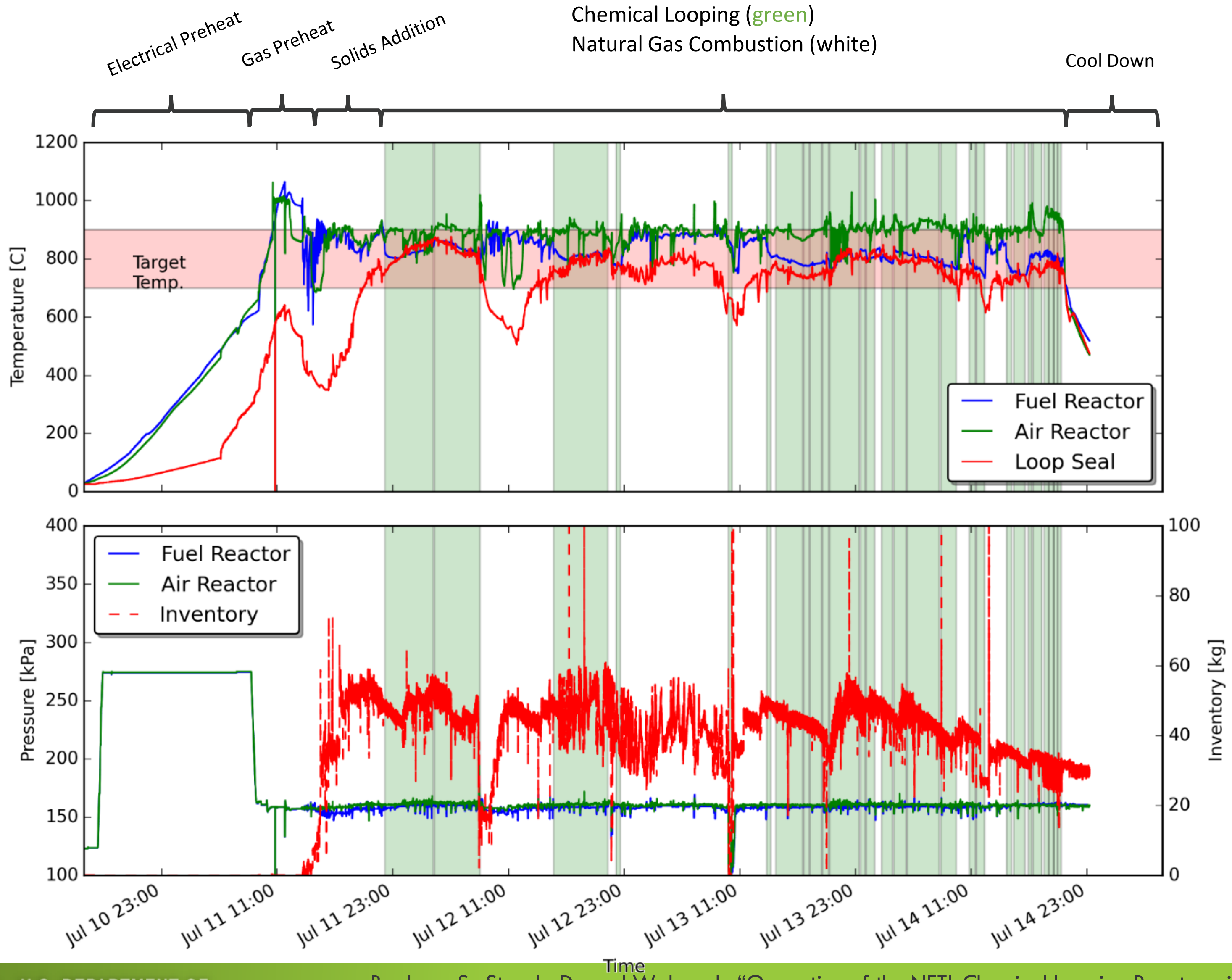
Hematite Carrier Chemical Looping Period



- Chemical looping tests began by transitioning from combustion mode in the fuel reactor (replacing air with nitrogen)
- Temperature in Fuel Reactor decays rapidly due to significant heat losses from the system and the endothermic reactions between CH_4 and hematite.
- Outlet gas concentration of CH_4 increases and the concentration of CO_2 decreases, and the methane conversion decreases

Weber, J.; Straub, D.; Bayham, S.; Breault, R.W., 2016. Operating Experience of a 50kWth Methane Chemical Looping Reactor. Proceedings of Fluidization XV, Montebello Quebec, Canada.

Carrier #3: Cu-Fe Material



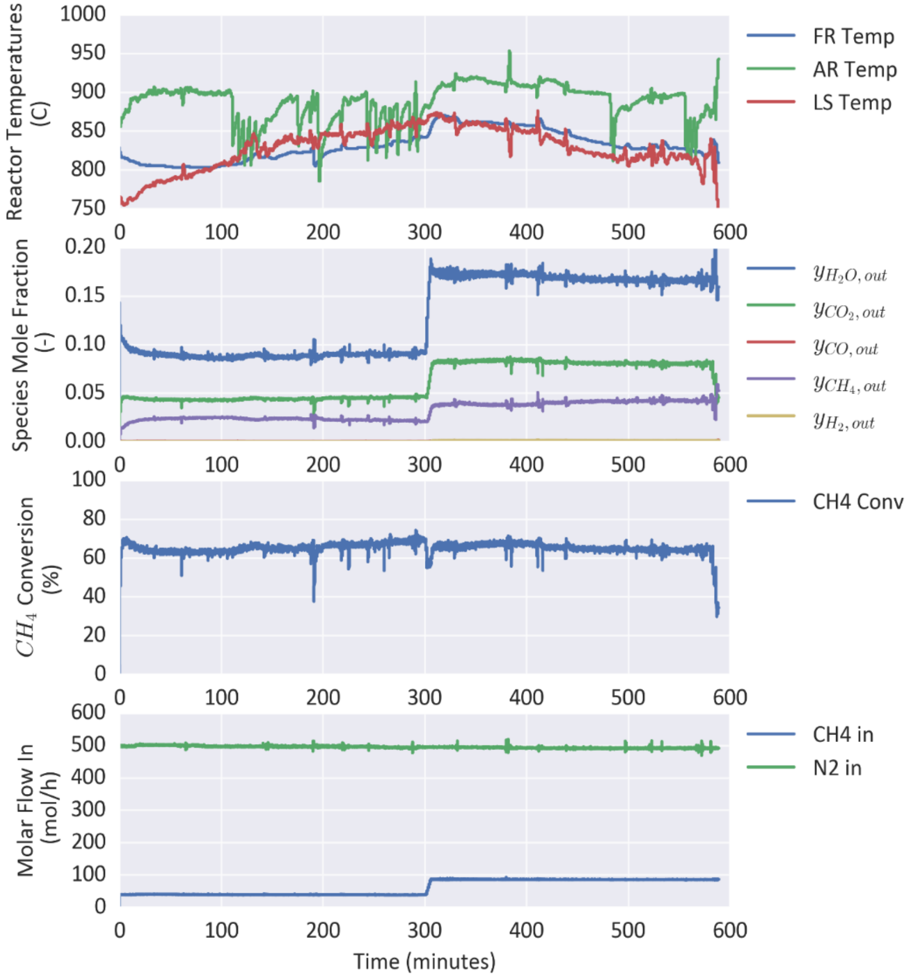
Fast Facts:

- Length:
  - 5 days, 10 h
- At Target Temp:
  - 4 days, 4 h
- CLC Mode (total):
  - 2 days, 3.7 h
- # of CLC Trials:
  - 26
- NG Feed to FR:
  - 6.7 – 50.0 kW_{th}
- NG Feed Concentration:
  - 5 – 42 vol.%
- 9 trials performed without natural gas combustion in AR
- Residence Times (Ranges)
  - Solid: 3.6 – 15.1 min
  - Gas: 0.48 – 1.26 s
- Methane Conversion to CO_2
  - 33.9% - 76.5%

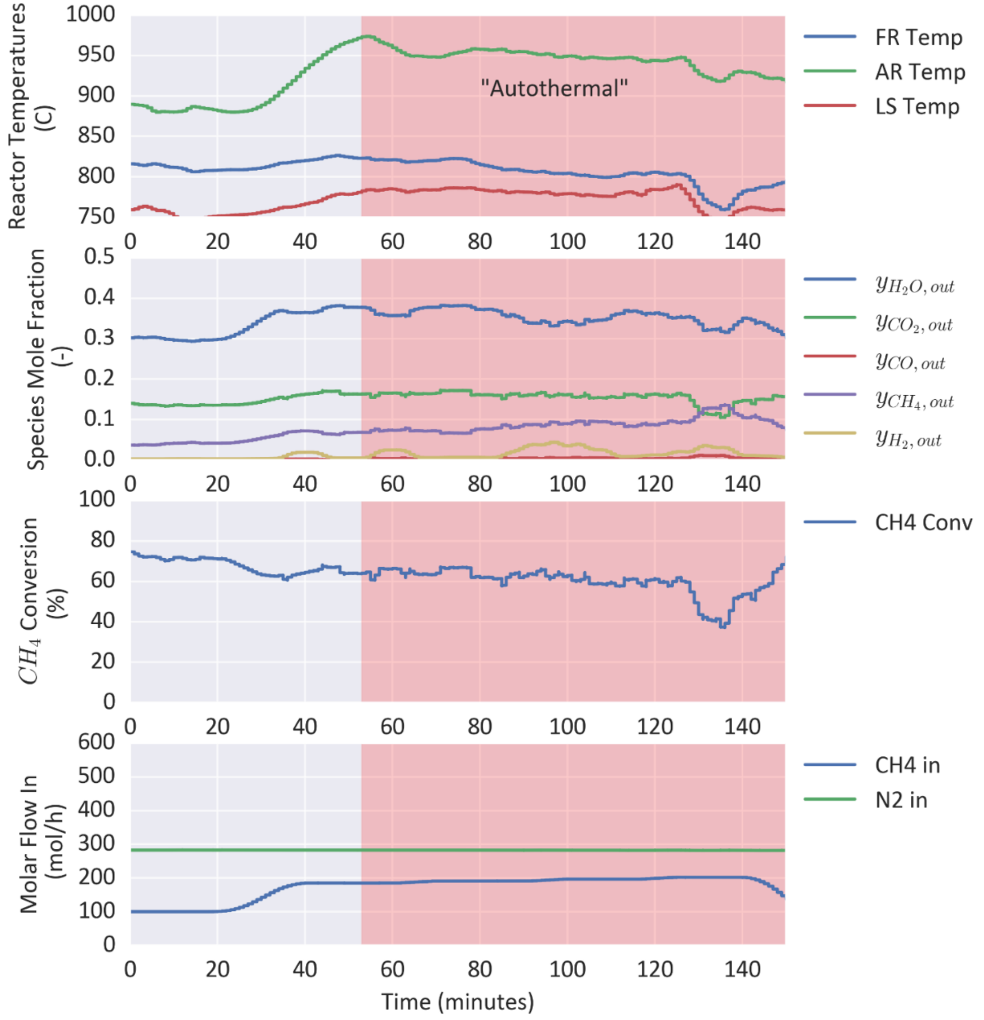
Bayham, S., Straub, D., and Weber, J., "Operation of the NETL Chemical Looping Reactor with Natural Gas and a Novel Copper-Iron Material," NETL-PUB-20912; NETL Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Morgantown, WV, 2017

Carrier #3: Performance Profiles

“Long term” test



“Autothermal” test



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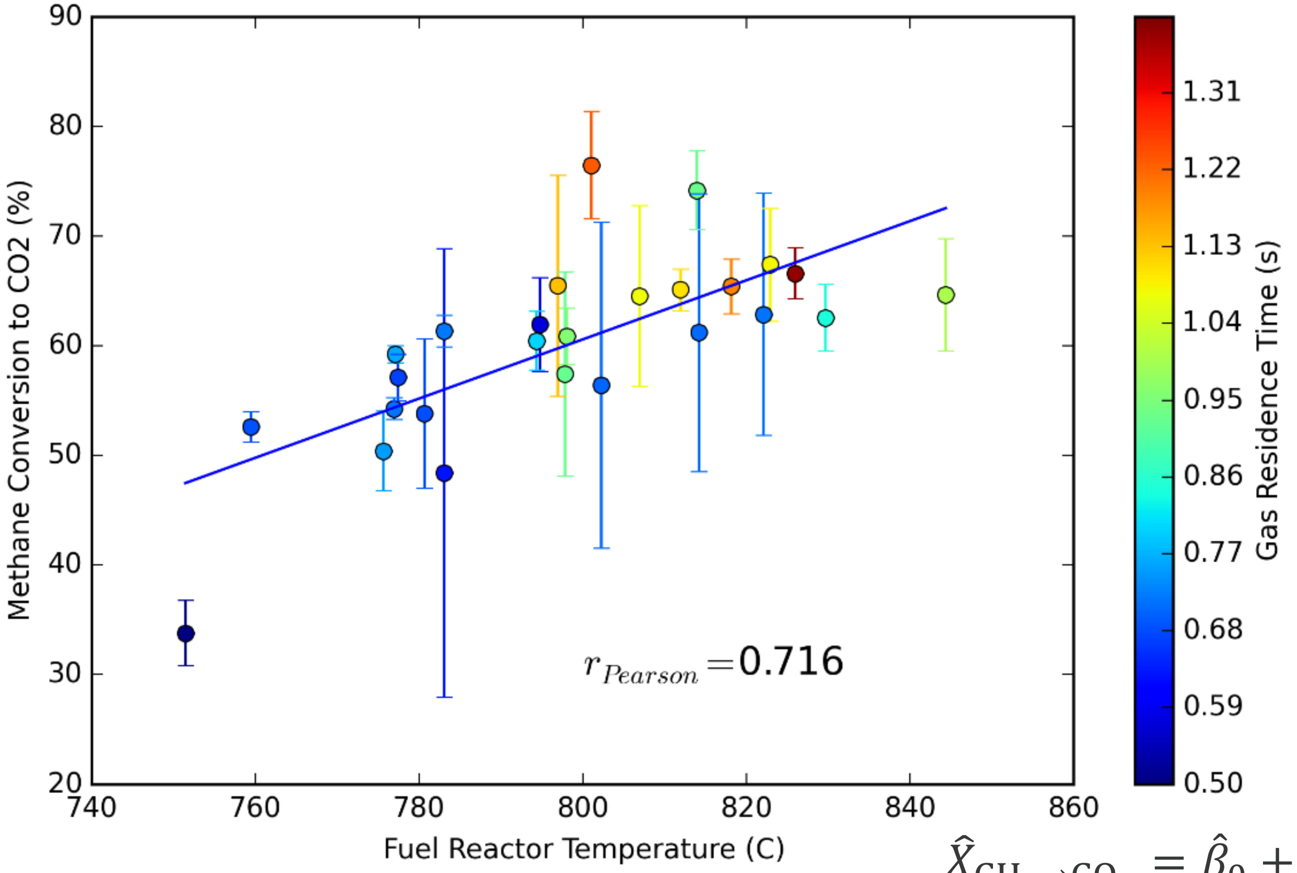
Carrier #3: Parametric Results



- Ordinary least squared analysis of five system parameters on the methane conversion:
  - Temperature, pressure, methane feed concentration, gas and solid residence times
- Independent variables "coded" to see weight of effect on methane conversion
- Statistically significant variables are temperature and gas residence time

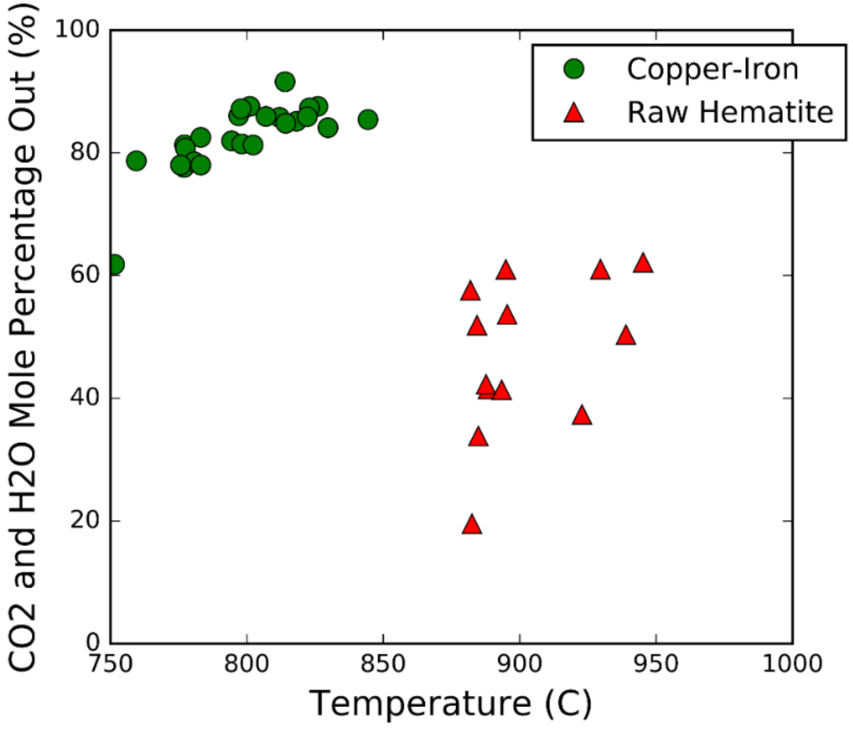
	Term	Coefficient	Standard Error	t-Statistic	P>|t|
Intercept	$\hat{\beta}_0$	0.6038	0.030	20.312	0.000
Temperature	$\hat{\beta}_1$	0.1085	0.038	2.876	0.009
Pressure	$\hat{\beta}_2$	-0.0288	0.029	-0.998	0.330
Concentration	$\hat{\beta}_3$	0.0188	0.033	0.577	0.570
Gas Residence Time	$\hat{\beta}_4$	0.0562	0.031	1.834	0.082
Solid Residence Time	$\hat{\beta}_5$	-0.0388	0.034	-1.128	0.273

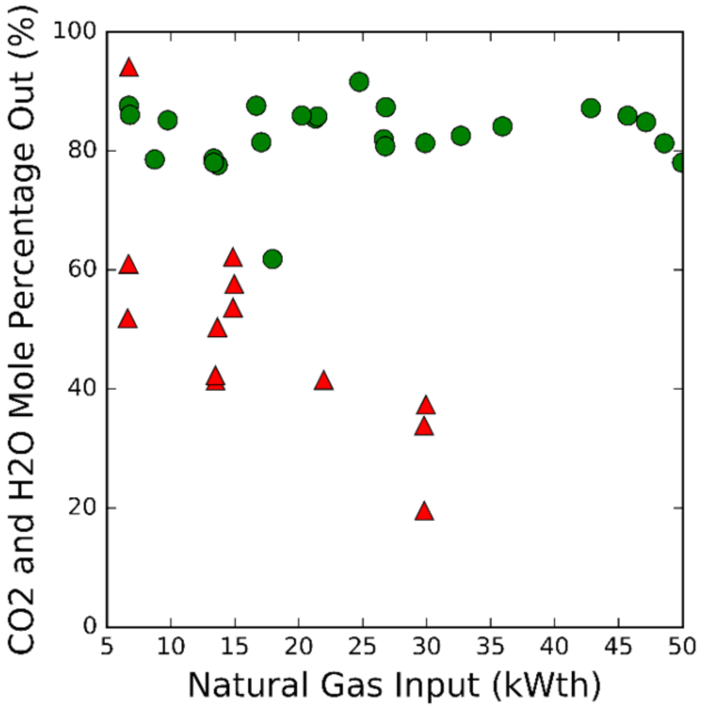
$$\hat{X}_{CH_4 \rightarrow CO_2} = \hat{\beta}_0 + \hat{\beta}_1 x_{Temp} + \hat{\beta}_2 x_{Press} + \hat{\beta}_3 x_{Conc} + \hat{\beta}_4 x_{\tau_{g,FR}} + \hat{\beta} x_{\tau_{OC,FR}}$$

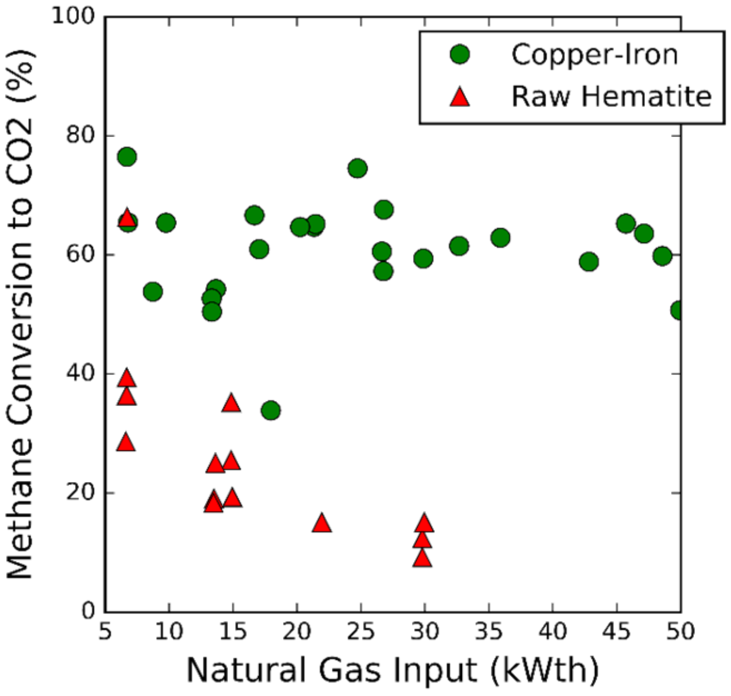
$$\hat{X}_{CH_4 \rightarrow CO_2} = 0.6038 + 0.1085 x_{Temp} + 0.0562 x_{\tau_{g,FR}}$$

Bayham, S., Straub, D., and Weber, J., "Operation of the NETL Chemical Looping Reactor with Natural Gas and a Novel Copper-Iron Material," NETL-PUB-20912; NETL Technical Report Series; U.S. Department of Energy, National Energy Technology Laboratory: Morgantown, WV, 2017

Hematite/CuFe Comparison





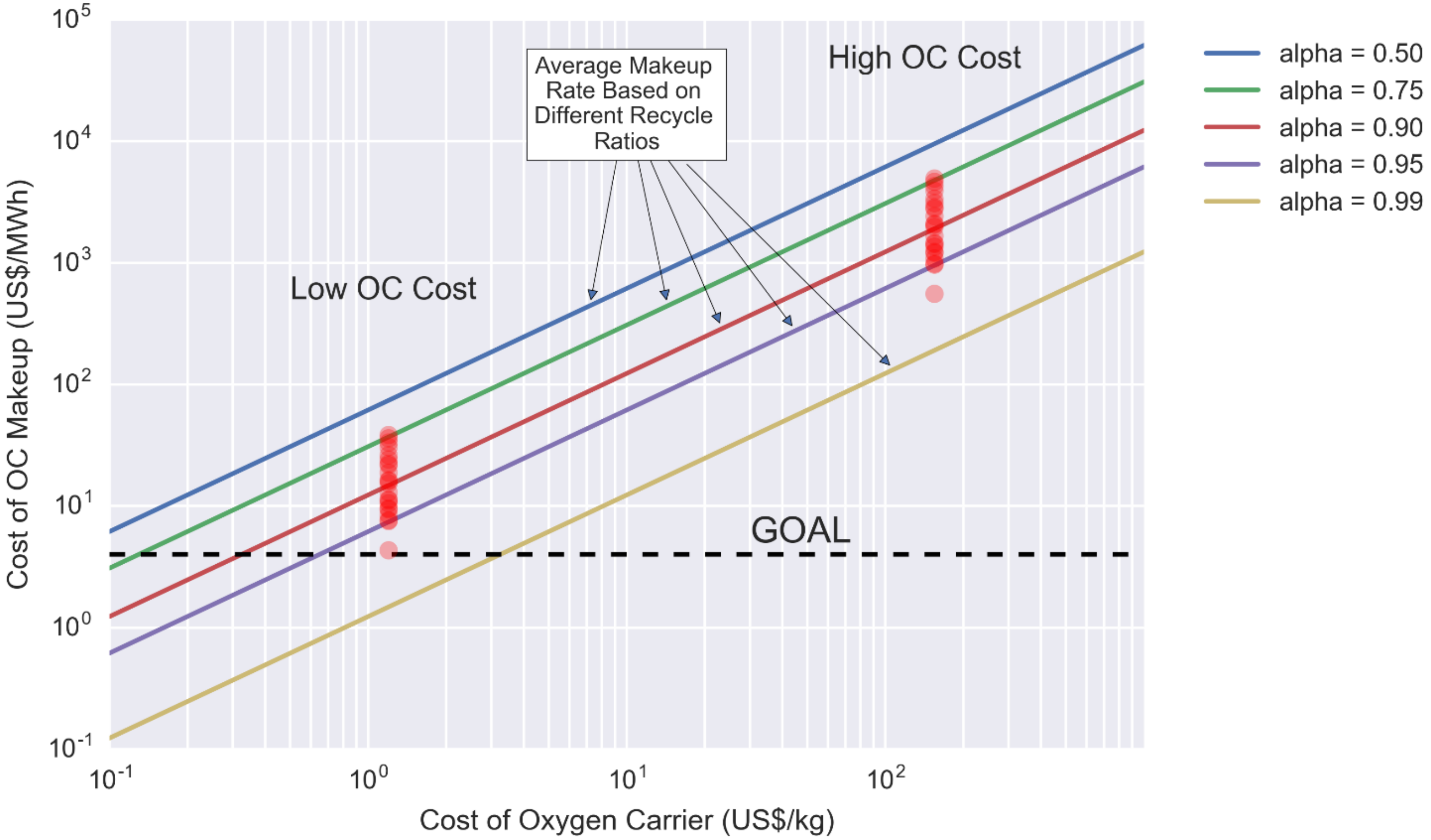


- The manufactured copper-iron material has a higher reactivity than the raw hematite ore even at a lower reaction temperature.
- Most CuFe trials have 90% mole percent CO_2/H_2O out!

- Increases in conversion may be stunted by the reactor design!
  - No matter how reactive the carrier
  - Due to mass transfer limitations in the fluidized bed

Bayham, S.; Weber, J.; Straub, D.; Breault, R. Performance Of A Raw Hematite and a Manufactured Copper-Iron Oxygen Carrier in a 50-kw Natural Gas Chemical Looping System" In: Proceedings of the Twelth International Conference on Circulating Fluidized Beds, Krakow Poland, May 2017.

Carrier #3: Sensitivity of Carrier Cost



- **Internal goal is a carrier makeup cost of $5/MWh**
- **High OC Cost: As-received from catalyst vendor**
  - Does not take into account economies of scale
- **Low OC Cost: Estimated cost using a scaled-up process**
  - Process modeled after taconite production
- **Red dots (data) are at 90% recycle rate at high and low OC cost assumptions**

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Challenges in scaling up…

- **Fluid beds can be difficult to scale!**
  - Performance may deteriorate as scale increases
- **What is the cost to make up the carrier?**
  - This has been determined to be the greatest factor in CLC plant economics[1]
- **Pressurized chemical looping**
  - Advantages due to more compact design
  - More auxiliary gases needed for same gas velocities (riser, loop seals, etc.)
- **Gas-Solids separation**

Table 2-15: Sensitivity parameter impacts expected on CLC reference system

Sensitivity Parameter	Vessel Height	Vessel Diameter	Circ. Rate	Boiler Eff.	Auxiliary Power	CO_2 Capture	Equip. Cost	Cost-of-steam
Oxygen carrier reactivity (relative to reference system)	Large –				Small –		Small –	Small –
Oxygen carrier loss (0 %) and price ($0/lb)								Large +
Oxygen carrier size (0.35mm) and density (203 lb/ft^3)	Small –				Small –		Small –	Small –
Oxygen carrier conversion (from reducer 53%; from oxidizer 95%)	Medium +		Large –		Small +		Small +	Small +
Reactor temperature (1700 °F)	Small –	Small +			Small –		Small –	Small –
Reactor velocities (reducer outlet 32 ft/s; oxidizer outlet 29 ft/s)	Large +	Large –			Small +		Small +	Small +
Natural gas conversion (97.5%)	Medium +			Small +	Small +	Large +	Small +	Small +
Oxidizer excess O_2 (3.6 mol% in off-gas)	Small –	Small +		Small –	Small +		Small +	Small +

Much can be learned from the successes/failures of similar technologies:

- Fluid catalytic cracking
- Fluid bed combustion
- Coal to liquids
- Gasification

[1]"ICMI CLC Techno-Economic Study with CLC Reactor Modeling." Report number URS-RES-1-1109, November 2014.

Summary

Performance of Hematite and Synthetic Copper-Iron Material

- Chemical looping tests utilized a natural hematite ore that has a relatively low reactivity, conducted at temperatures that ranged from 850 – 1000°C.
- The oxygen carrier circulation rates for these tests were on the order of 400 kg/hr, and the conversion of methane to carbon dioxide ranged from 10-50%.
- The fuel reactor temperature and the bulk gas residence time through the fuel reactor bed are two factors that have a significant effect on the observed fuel conversion.
- The hematite oxygen carrier material seems to be a very durable mineral for chemical looping combustion applications, but the reactivity is very poor.
- There are also some indications that this material could experience some agglomeration issues if the operating temperature exceeds 1000°C.

- Copper-iron material was circulated/reacted at temperature (700-850°C) for over four days
  - Copper-iron material has better conversion than hematite even running at a lower temperature
- Twenty-six trial chemical looping trial periods were performed (40 h total)
  - Nine tests were performed without NG addition to air reactor (5 h)
  - The last four periods of the campaign performed without NG in the air reactor *and* electric preheat (1.6 h). Conversion and temperature were fairly stable, but longer periods are required to verify results.
- Estimated makeup cost is \$560-5000/MW_{th}-hr, which is higher than the \$5/MW_{th}-hr target (even with assumed 90% recycle rate)
- This number can be improved as the carrier production is scaled up

Concluding Remarks

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- **Despite 20+ years of study, there are still many unanswered questions regarding the feasibility of CLC**
  - With further effort, conversion of fuel could be improved, but how to maintain performance upon scaleup?
  - Carrier makeup cost is a very important parameter, but the scaled cost is unknown
- **CO_2 is a low-value product!**
  - If we could produce something more valuable than electricity/CO2, then financial risk could be lowered, and the conversions might not need to be as high

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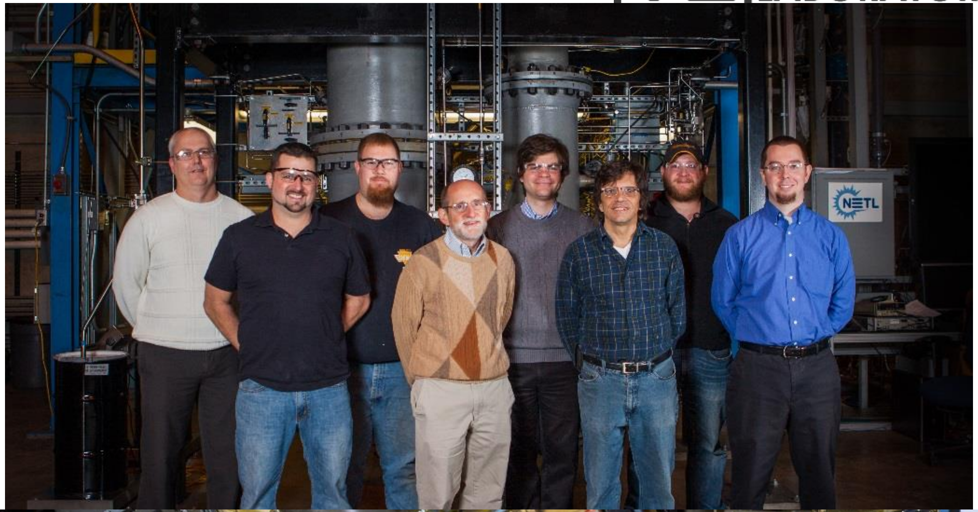

Thank you for your attention!

Questions?

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